Intrinsically-Catalytic Single-Chain Polymeric Nanoparticles showing Pseudo-Polymerase Behavior

Jose A. Pomposo, Centro de Fisica de Materiales (CSIC, UPV/EHU)-Materials Physics Center, UPV/EHU and IKERBASQUE

Irma Perez-Baena, Centro de Fisica de Materiales (CSIC, UPV/EHU)-Materials Physics Center

Fabienne Barroso-Bujans, Centro de Fisica de Materiales (CSIC, UPV/EHU)-Materials Physics Center

Urs Gasser, Laboratory for Neutron Scattering, Paul Scherrer Institut

Arantxa Arbe, Centro de Fisica de Materiales (CSIC, UPV/EHU)-Materials Physics Center

Angel J. Moreno, Centro de Fisica de Materiales (CSIC, UPV/EHU)-Materials Physics Center

Juan Colmenero, Centro de Fisica de Materiales (CSIC, UPV/EHU)-Materials Physics Center, UPV/EHU and DIPC

Single-chain nanoparticles have recently gained prominence in nanoscience and nanotechnology due to the exceptional and sometimes unique properties displayed by such soft nanoobjects (1-5). As individual self-collapsed coils, single-chain nanoparticles mimic the structure of folded biomacromolecules although in a rough, primitive manner. Previously, bioinspired catalytic nanoobjects have been demonstrated based on a variety of molecular structures and nanoentities such as macrocyclic compounds, star and helical polymers, dendrimers and micelles. However, the construction of bioinspired catalysts based on folded/collapsed single polymer chains is challenging due to the polydisperse nature (in size and composition) of current synthetic polymers and the lack of efficient folding protocols.

In this oral contribution we present our recent results concerning catalyst-assisted chain folding/collapse with concurrent catalyst immobilization giving rise, in a single step, to intrinsically catalytic single-chain nanoparticles (IC - SCNPs). Moreover, we report the synthesis, characterization and properties of IC-SCNPs displaying unprecedented pseudo-polymerase catalytic activity. Single-chain nanoparticle formation through an intramolecular folding mechanism was supported by SEC, 1H NMR, AFM, DLS and TEM results. During this process, that completed after less than 3 h of reaction time, B(C6F5)3 moieties were found to be immobilized / entrapped by the collapsing single-chain nanoparticles as supported by TGA, 19F NMR and XPS measurements while retaining their catalytic activity. Combined SANS measurements and MD simulations revealed a relatively open morphology for the IC-SCNPs under good solvent conditions, which seems to be beneficial for facilitating access of the reagents to the active catalytic sites.

We have explored with success the use of IC-SCNPs in two different synthetic applications: i) borane–catalyzed reduction of beta-diketones to silylprotected 1,2-diols with a maximum turnover frequency of 5,880 h-1 for IC-SCNPs having Mw $<$ 100 kDa, and ii) unprecedented pseudo-polymerase-like ROP synthesis of high-molecular-weight poly(THF). We use the term "pseudo-polymerase behaviour" to avoid confusion with the exquisite activity of natural polymerase enzymes that use templates (mRNA, DNA) to synthesize perfectly defined (in length and sequence) biomacromolecules.

In summary, we have developed a simple and efficient method allowing catalyst-assisted single chain folding/collapse with concurrent catalyst immobilization giving rise, in a one-pot fashion, to IC-SCNPs displaying pseudo-polymerase behavior. This new pathway to metal-free, catalytic soft nano-objects has been realized by using glycidylic-decorated polymers as soft nanoparticle precursors and B(C6F5)3 as a highly-efficient catalyst.

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